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The Low Frequency Raman Spectra of Ammonium Halides  
in the Disordered Phases I and II<sup>\*</sup>

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**CASE FILE  
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## INTRODUCTION

The ammonium halides are well known to undergo a number of structural modifications. The various crystallographic structures and transition temperatures have been established<sup>(1-6)</sup>. At atmospheric pressure, the different known phases are referred to as phases I, II, III and IV in order of the decreasing temperatures. In the disordered phases I and II, the ammonium ions are randomly distributed between energetically equivalent orientations. In phase I, the arrangement of the ammonium and halide ions in the lattice is the same as in the NaCl crystal (space group  $O_h^5$ ) while phase II has a structure of the CsCl type (space group  $O_h^1$ ). Phases III and IV are the ordered ones. A small distortion along one of the cubic symmetry axes causes the transformation to the tetragonal structure of phase III which contains two "molecules" per unit cell. The ammonium ions are parallel-oriented along the "z" axis but are antiparallel-oriented in the xy plane perpendicular to the tetragonal axis. The space group of phase III is  $D_{4h}^7$ . In phase IV, we have again a cubic lattice of the CsCl type, with all the ammonium ions parallel-oriented along the three-fold axis of the cubic lattice; the space group is  $T_d^1$ .

The bromide presents all these modifications at atmospheric pressure, while the tetragonal antiparallel phase is not known for the chloride and the CsCl ordered phase does not appear with the iodide at atmospheric pressure. A mapping of the phase transitions in the different ammonium halides at atmospheric pressure is given in Ref. 20.

A lot of spectroscopic investigations have been carried out by inelastic neutron scattering measurements<sup>(7-14)</sup>, by infrared transmission<sup>(16-20)</sup> and reflection<sup>(20)</sup> and by Raman scattering experiments<sup>(19-30)</sup>. The spectra of the ordered phases III and IV are well known and well understood on the basis of factor group analysis. Additional features appear in the infrared

basis of factor-group analysis. Additional features appear on the infrared spectra of the chloride and the bromide in phase II, near the  $\nu_4$  triply degenerate bending mode of the ammonium ions, and are shown to be induced by the disorder<sup>(17,18)</sup>. Group theoretically inactive modes appear also for all the ammonium halides in phase II in the low frequency region of the Raman spectra corresponding to the external modes of the crystals. Wang et al. have studied the temperature dependence of the lowest frequency peak of the chloride and the bromide, above and just below the order-disorder phase transition temperature. They concluded that this additional peak in the bromide can be interpreted in terms of short-range ordering<sup>(27)</sup>, but for the chloride this short-range ordering is less important<sup>(28)</sup>. Such an analysis has not been made for the iodide in the disordered phases I and II, and no spectroscopic data is available for the chloride and the bromide in phase I. On the other hand, no attempt has been made in order to explain the spectra of the disordered phases on the basis of group theoretical considerations.

We report in this work new Raman scattering data of the ammonium halides in both disordered phases I and II. The effect of disorder and that of short-range ordering is discussed in terms of group theoretical arguments.

## EXPERIMENTAL

The Raman spectra have been recorded using a Spex double monochromator with photon-counting detection, and a Coherent Radiation Model No. 52 argon-ion laser, operating with the  $4880\text{\AA}$  and  $5145\text{\AA}$  lines. Right angle and back scattering geometry have been used.

The single crystals of ammonium chloride and bromide came from Prof. C. W. Garland, Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology. The ammonium iodide single crystals were grown from saturated aqueous solutions.

The spectra at high temperature have been obtained with a small heating unit, by placing the single crystals in a bath of diffusion pump oil. This procedure has the advantage to avoid the sublimation of the samples at high temperature and to provide a good temperature control. The only observable effect of the oil bath on the Raman spectra is a little increase of the background intensity.

## RESULTS

We have recorded the Raman spectra of ammonium chloride, bromide and iodide single crystals at room temperature with polarized incident and scattered lights. The chloride and the bromide are in phase II while the iodide is in phase I at room temperature. We have also obtained the spectra of the chloride and that of the bromide at high temperature, above the phase II to phase I transformation temperature ( $457.7^{\circ}\text{K}$  for the chloride and  $411.2^{\circ}\text{K}$  for the bromide). It appears that the crystals become multidomained above this transition temperature. For the iodide, there is only a very little temperature range corresponding to phase II ( $225.8^{\circ}\text{K} - 231.8^{\circ}\text{K}$ ). Since the iodide crystals also break on cooling from phase I to phase II and some data have already been obtained in phase II with polycrystalline samples<sup>(19,20)</sup> we did not repeat these experiments.

### $\text{NH}_4\text{Cl}$ and $\text{NH}_4\text{Br}$ phase II

The Raman spectra of these samples depend on the polarization of the lights and on the orientation of the crystal with respect to the incident and the scattered beams. But, for a given orientation of the crystal, the same results are obtained using either right angle or back scattering geometries.

In the low frequency region corresponding to the external modes, the Raman spectrum of the chloride at room temperature is composed of five peaks whose frequencies are 95, 115, 145, 170 and  $195\text{ cm}^{-1}$ . With the bromide in the same conditions, only four distinct peaks appear at 56, 80, 137 and  $180\text{ cm}^{-1}$ . These results are in good agreement with the previous works<sup>(19-30)</sup>.

For cubic crystals, the Raman active representations are of A, E and F types. With the usual  $90^{\circ}$  geometry, the incident and scattering lights have been selected as described by Krauzman<sup>(31)</sup> to enable separate observation

of the phonon symmetries. If the X, Y and Z directions correspond to the principal axes of the crystal, the Z(xx)Y configuration allows  $A + 4E$  while the other crossed configurations allow F alone. If the a, b and c directions refer respectively to the 110,  $\bar{1}10$  and 001 directions of the crystal, then the a(bb)c configuration allows  $A + E + F$ , a(ba)c 3E, a(cb)c and a(ca)c F.

The peaks of the chloride at 115, 145, 170 and  $195\text{ cm}^{-1}$  and those of the bromide at  $\sim 80$ , 137 and  $180\text{ cm}^{-1}$  correspond to the F type since they are observed with the Z(xz)Y, Z(yx)Y, Z(yz)Y, a(bb)c, a(cb)c and a(ca)c configurations only. The peak of the chloride at  $95\text{ cm}^{-1}$  and that of the bromide at  $56\text{ cm}^{-1}$  appear only with the Z(xx)Y, a(bb)c and a(ba)c configurations. They correspond unambiguously to the E type, but it is also possible that they receive a contribution of an A component. If these peaks were purely E, the depolarization ratio between the a(bb)c and a(ba)c configurations should be 0.33. For a comparison, we have measured this ratio for the peak of the chloride observed at  $1710\text{ cm}^{-1}$ , which corresponds to the type E bending mode of the ammonium ions, and we found 0.39 in good agreement with the theoretical value. The value 0.66 obtained for the peak at  $95\text{ cm}^{-1}$  allows us to think that an A component contributes to the scattered intensity at  $95\text{ cm}^{-1}$  and that its intensity is of the same order of magnitude as the E component. With the bromide, unfortunately, the quality of the sample was not good enough to enable us to determine unambiguously if there is a contribution coming from an A component in the peak at  $56\text{ cm}^{-1}$ .

TABLE I - Low frequency Raman spectra of the ammonium halides in phase II.

$\text{NH}_4\text{Cl}$ (300°K)		$\text{NH}_4\text{Br}$ (300°K)		$\text{NH}_4\text{I}$ (240°K)*
Frequency ( $\text{cm}^{-1}$ )	Type	Frequency	Type	Frequency
95	A + E	56	A(?) + E	
115	F	~80	F	
145	F	137	F	125
170	F			
195	F	180	F	160

\* See Ref. 20.

The spectra obtained at high temperature below the phase II to phase I transformation temperature show a decrease of the Raman intensity in the low frequency region, accompanied by an increase of the background intensity. For the chloride, we also notice a progressive disappearance of the peak at  $170\text{ cm}^{-1}$  with respect to the other peaks, as the temperature is raised up. At about  $440^\circ\text{K}$  this peak has completely disappeared while the other peaks at 95, 115, 145 and  $195\text{ cm}^{-1}$  are still present and quite well observable, but broader than at room temperature. With the bromide

NH<sub>4</sub>Cl, NH<sub>4</sub>Br and NH<sub>4</sub>I phase I

As it has already been mentioned, the NH<sub>4</sub>Cl and NH<sub>4</sub>Br single crystals, in phase II at room temperature, become multidomained above the phase II to phase I transition temperature, but we have obtained the spectrum of NH<sub>4</sub>I single crystal in phase I at room temperature.

The low frequency Raman spectra of all the ammonium halides in phase I are almost featureless. All we can see are very weak and broad bands at about 100 and 160 cm<sup>-1</sup> with the chloride, with the bromide and 125 cm<sup>-1</sup> with the iodide. These bands are almost indiscernible from the background and it was not possible to determine their symmetry type. These new results with the chloride and the bromide in phase I are very similar to what had already been observed with the iodide<sup>(19,20,23,24)</sup>.



## DISCUSSION

### I - Selection Rules

Because of the disorder in the ammonium ions orientations of phases I and II, one usually considers the ammonium ions as having a cubic symmetry, so that they occupy  $O_h$  sites in the lattice. Thus, the space group of phase II (disordered cubic of the CsCl type) is  $O_h^1$  and that of the phase I (disordered cubic of the NaCl type) is  $O_h^5$ . Under these assumptions, the optical phonons belong to the  $F_{lu}$  type for both phases I and II, so that they are infrared active but Raman inactive at wave-vectors  $k \approx 0$ , corresponding to the  $\Gamma$  point, the center of the Brillouin zone. This approximation seems to be good for phase I since only very weak features are observed, but is not convenient for phase II, where strong scattering arises in the phonon frequency region.

The space group of phase II is not exactly  $O_h^1$  since the ammonium ions have always a tetrahedral symmetry, but is " $T_d^1$  disordered". There is a breakdown of the translational invariance of the crystal and so, we expect because of the breakdown of the  $k$  conservation rule, a spectrum which reflects the one phonon density of states<sup>(32-34)</sup>. The spectrum of  $NH_4Cl$  observed at room temperature is in good agreement with the one phonon frequency distribution calculated by Cowley for  $NH_4Cl$  and  $ND_4Cl$  in the  $T_d^1$  ordered phase<sup>(14)</sup>, and the three mean peaks at 95, 145 and  $170\text{ cm}^{-1}$  can be very well correlated with the three maxima of the calculated one phonon density of states.

In order to explain the observed polarization of the Raman spectra in phase II, we have to find the selection rules in this disordered phase, by considering the symmetry properties of optical and acoustical phonons in the different branches of the Brillouin zone. To do that, we shall refer to the model introduced by Loveluck and Sokoloff for disordered crystals<sup>(33,34)</sup> and we shall apply the method used for crystals sloped by impurities<sup>(35)</sup>, assuming

here that the impurity is due to the ammonium ions themselves since the breakdown of the translational invariance of the crystal is due to the disorder in their orientation. So, we have to construct the space-group representations from the corresponding wave-vector group representations<sup>(36)</sup>, using the method described by Koster<sup>(37)</sup> and applied by Loudon for the sodium chloride, diamond and zincblende lattices<sup>(35)</sup>.

In the model of Sokoloff<sup>(33,34)</sup>, in place of the polarizability of the crystal, the polarizability of a single  $\text{NH}_4^+$  enters the expression for the cross-section in the disordered phase. This polarizability tensor has an index  $\sigma$ , in addition to the tensor indices, to specify the orientation of the  $\text{NH}_4^+$  site. The halide ions in the disordered phase occupy  $O_h$  sites, whereas the nitrogen site has a tetrahedral symmetry because of the four hydrogen surrounding it. If we place the origin to which the symmetry operations are referred at a halide ion site, the factor-group of the disordered crystal would be  $O_h$ . Since some operations of this group would change the index  $\sigma$  on the polarizability of a particular  $\text{NH}_4^+$  ion, this tensor will not transform as a tensor under the  $O_h$  group. But, if we choose the origin to be at a nitrogen site, the point group of the lattice is  $T_d$ , because the hydrogen of that particular nitrogen must be invariant. Thus, with this choice of origin, it is possible to apply the usual arguments of examining whether the various symmetry of phonons are contained in the tensor.

The symmetry properties of the optical and acoustical branches of ammonium chloride in the ordered cubic  $T_d$  structure have been tabulated by Cowley<sup>(14)</sup> by making the choice of the origin to which the symmetry operations are referred on the halide ion. As a consequence of the choice of origin we have made (nitrogen site) the appropriate labels for the various optical and acoustical modes given by Cowley must be interchanged<sup>(38)</sup>. This is of

importance only for the X, M and Z points where the optical and acoustical modes do not belong to the same symmetry types, but for all the other points in the Brillouin zone the labels are the same as those given by Cowley, since at these points the optical and acoustical modes have respectively the same symmetry types. Table II shows the symmetry properties of phonons in the  $T_d^1$  lattice of ammonium chloride, with the origin taken at a nitrogen site. We utilize here the usual notations given for example in Ref. 39 (for a comparison of the different notations used in the literature, see for example Ref. 40).

The results of the calculation of the space group reduction coefficient for the ammonium halide  $T_d^1$  lattice are given in table III. If we consider the disordered crystal to be a perfect ordered lattice  $T_d^1$  of right oriented ammonium ions containing 50% of left oriented ammonium ions as impurity, randomly distributed in the cation sites of the crystal, we can find the Raman selection rules of the disordered phase II of  $NH_4Cl$  by a comparison of tables II and III. The Raman active phonons must contain the  $A_1$ , E or  $F_2$  representations and have the corresponding polarization characters. These results are given in table IV.

The selection rules for the ammonium halides phase I can be obtained in a similar way, by considering the space group reduction coefficients of the NaCl structure<sup>(35)</sup> and the symmetry properties of optical and acoustical phonons<sup>(35,41)</sup> assuming that the dispersion curves of NaCl are similar to those of the ammonium halides phase I (this must be a good approximation considering the fact that the mass of the  $Na^+$  and  $NH_4^+$  ions is almost the same). Here again, we must make the choice of the origin at a nitrogen site, so that the labels of the optical and acoustical modes given in Refs. 35, 41 are the same as ours. Furthermore, we have also to perform the calculation of restricting the symmetry

from that of the space group  $O_h$  to that of the site group  $T_d$  of the  $NH_4^+$  ions, which is easily done with the correlation tables<sup>(39)</sup>. Table V shows the Raman selection rules for the phonon modes in the ammonium halides phase I.

## II - Analysis of the Spectra

Tables IV and V show that all the phonon modes can be Raman active for both the disordered phases I and II, but they must present different polarization characters due to their different symmetry properties in the branches of the Brillouin zone.

By considering the dispersion curves of ammonium chloride<sup>(12-14)</sup> and the results of table IV, we can correlate the maxima observed on the Raman spectrum of  $NH_4Cl$  phase II with phonon modes in the Brillouin zone corresponding to wave-vectors  $k \neq 0$ . The same correlations can be tentatively established for the bromide and the iodide phase II, if we assume that the shapes of the dispersion curves are similar to those of the chloride. The results of this assignment are shown in table VI.

So, according to their polarization character and to their frequency, all the maxima and shoulders observed on the Raman spectra of ammonium halides in phase II can be assigned to different optical and acoustical phonon modes at high symmetry points in the Brillouin zone (table VI). But, with such an explanation, since the observed peaks present a well-defined polarization character, we must assume that a lot of phonon modes which have both characters of crossed and uncrossed polarization (table IV), do not contribute to the Raman scattering. At least, we must assume that only the F component of the Raman tensor gives rise to scattering by optical phonons and that only the A + E components contribute to the scattering by acoustical phonons. In other words, the spectra do not reflect exactly the one phonon density of states

but show only resonant modes corresponding to phonons at high symmetry points in the Brillouin zone. Two kinds of arguments can be considered in order to explain this phenomenon.

1) The maxima observed on the Raman spectra correspond effectively to maxima of the frequency distribution<sup>(14)</sup>. On the other hand, the Raman scattering intensity has the frequency dependence of the ordered crystal density of states weighted by the frequency dependent amplitude of vibration squared. So, assuming that the one phonon density of states of the lattice is weighted by a strongly frequency depending amplitude, it may be possible to understand the spectra of ammonium halides phase II in terms of phonons at high symmetry points of the Brillouin zone. However, there are still some difficulties:

a) We cannot explain the behavior of the peak observed at  $170\text{ cm}^{-1}$  with the chloride phase II. This frequency can be assigned to the TO(F) and/or LO, TO(R) and/or LO,  $T_1^0$ (M) modes (table VI), and the corresponding maximum disappears progressively on heating the sample in phase II, while all the other features of the spectrum remain almost unchanged. On the other hand, no similar peak is observed with  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{I}$  phase II, the TO(F) mode frequency being determined by infrared absorption respectively at  $147$  and  $143\text{ cm}^{-1}$  (20).

b) It is difficult also to understand the fact that in phase I, the spectrum resembling the one phonon density of states disappears almost completely with all the ammonium halides, whereas disorder also occurs in this phase and all the phonon modes can also be Raman active (table V).

2) We can also consider that the mechanism which enhances the scattering by phonons at high symmetry points in the Brillouin zone is due to the presence of short-range ordering in the disordered phase II. Such an argument has already been considered by Wang et al.<sup>(26-28)</sup> and theoretically by

Sokoloff<sup>(34)</sup>. By this way, Wang explained the behavior of the low frequency peak at  $56 \text{ cm}^{-1}$  in  $\text{NH}_4\text{Br}$  near the phase III to phase II transition temperature<sup>(26,27)</sup>, but Wang concluded that the short-range ordering does not contribute totally to the corresponding band observed at  $95 \text{ cm}^{-1}$  with  $\text{NH}_4\text{Cl}$ <sup>(28)</sup>.

In phase II, the three-fold axes of the  $\text{NH}_4^+$  ions coincide with those of the cubic sublattice of the halide ions. So, they have only two energetically equivalent orientations. It is easy to imagine some short-range correlation can occur, so that parallel or antiparallel short-range ordering can be present in phase II. The transition from phase II to the tetragonal phase III involves a halving of the Brillouin zone which replaces the M point of the cubic lattice at the zone center of the tetragonal one. The calculations of Sokoloff show that there should be strong Raman scattering from phonons near the M point of the Brillouin zone, enhanced by such an antiparallel short-range ordering<sup>(34)</sup>. The dispersion curves<sup>(12,13)</sup> and our group theoretical considerations show that we can reasonably assign the maxima observed at  $95, 115, 145$  and  $195 \text{ cm}^{-1}$  with  $\text{NH}_4\text{Cl}$  phase II to phonon modes at the M point of the Brillouin zone (table VI); this is consistent with Sokoloff's point of view<sup>(34)</sup>. In a similar way, the peaks at  $56, 80, 137$  and  $180 \text{ cm}^{-1}$  of  $\text{NH}_4\text{Br}$  and those of  $\text{NH}_4\text{I}$  at  $125$  and  $160 \text{ cm}^{-1}$  can also be assigned to the phonon modes at the M point (table VI). According to this assignment, in the pure phase III, the frequencies of the phonon modes which can be regarded as zone boundary modes of the phase II cubic lattice are observed at  $62, 75, 133$  and  $179 \text{ cm}^{-1}$  with  $\text{NH}_4\text{Br}$  and at  $45, 57, 123$  and  $155 \text{ cm}^{-1}$  with  $\text{NH}_4\text{I}$ <sup>(20)</sup>.

Besides, if we consider now that a parallel short-range ordering, similar to the ordering existing in phase IV can enhance the scattering by phonons at the zone center in phase II, we account for the maximum observed at  $170 \text{ cm}^{-1}$  with  $\text{NH}_4\text{Cl}$  phase II by the assignment  $\Gamma(\text{TO})$ .

So, after these considerations, we find antiparallel short-range ordering to be present for all the ammonium halides in phase II, while the parallel one appears only in  $\text{NH}_4\text{Cl}$ . This may be explained by the fact that phase II  $\text{NH}_4\text{Cl}$  occurs just after the parallel ordered phase IV, while with the bromide, we must go through the antiparallel ordered phase III before reaching phase IV at very low temperature.

When we heat  $\text{NH}_4\text{Cl}$  in phase II, after this interpretation, the parallel short-range ordering progressively disappears, while the antiparallel one is still present. Again, this is consistent with the fact that the pure antiparallel ordered phase occurs at higher temperature than the parallel ordered.

We are also able to understand why in phase I, only a very weak spectrum is observed with all the ammonium halides in the low frequency region. Couture-Mathieu and Mathieu<sup>(23,24)</sup> have shown, by measuring the depolarization ratio of the Raman peak of  $\text{NH}_4\text{I}$  phase I at  $1630\text{ cm}^{-1}$ , corresponding to the doubly degenerate bending mode of the  $\text{NH}_4^+$  ions, that one three-fold axis of the ammonium ions coincides with one of the four-fold axes of the cubic lattice of the halide ions. So now, in phase I, the ammonium ions have six energetically equivalent orientations so that it is more difficult than in phase II to imagine a short-range ordering to be present. Furthermore, the measured depolarization ratio agrees well with the calculated one assuming that all the possible orientations occur with an equal probability<sup>(23,24)</sup>. We expect that the crystal is very much more random in phase I than in phase II. The short-range ordering which enhances scattering by phonons at special points in the Brillouin zone is now a lot less probable, and so, the resulting phonon spectra of phase I are a lot less intense than those of phase II.

Remarks

1. We can also imagine another type of antiparallel short-range ordering, similar to the ordering which has been suggested by Garland et al. for a new high pressure phase of  $\text{NH}_4\text{Br}$ <sup>(42)</sup>. In this hypothetical antiparallel ordered tetragonal phase, whose space group might be  $D_{4h}^{10}$ , there is a halving of the Brillouin zone of the cubic lattice of phase II, which replaces the zone center of the tetragonal lattice at the X point. If such a short-range ordering is present in phase II, we expect an enhancement of the scattering by phonons at the X point of the Brillouin zone. Table VI shows that such a hypothesis can account for all the observed peaks, except that of the chloride at  $95\text{ cm}^{-1}$  and that of the bromide at  $56\text{ cm}^{-1}$ . The only phonon mode at X with a  $A + E$  polarization character is  $1A(X)$  (table IV), located at about  $175\text{ cm}^{-1}$  with  $\text{NH}_4\text{Cl}$ <sup>(12-14)</sup> and so expected for the bromide at higher frequency than  $56\text{ cm}^{-1}$ .

2. The pressure dependence of the Raman peak of  $\text{NH}_4\text{Cl}$  phase II at  $170\text{ cm}^{-1}$  has been measured by Nicol et al.<sup>(29)</sup>. We have found exactly the same pressure dependence for the  $\text{TO}(\Gamma)$  band at  $172\text{ cm}^{-1}$  by infrared absorption where it is group theoretically active in phase II. So, the assignment of the Raman peak of  $\text{NH}_4\text{Cl}$  phase II at  $170\text{ cm}^{-1}$  to  $\text{TO}(\Gamma)$  is supported by these results.



## CONCLUSION

We have established the Raman selection rules of the ammonium halides in the disordered phases I and II, on the basis of the model of disordered crystals introduced by Sokoloff and Loveluck, and by group theoretical considerations. The observed phonon Raman spectra of phase II can be assigned to phonon modes at high symmetry points of the Brillouin zone. The best understanding of the spectra is given by the hypothesis according to which the mechanism which enhances the scattering by phonons at special points of the Brillouin zone is due to short-range ordering present in phase II, and that such a mechanism does not occur in phase I which might be a lot more disordered than phase II. However, it is also quite possible that the effect of disorder also contributes to the phonon spectra of phase II.

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TABLE II - Symmetry properties of the phonon branches of the dispersion curves in ammonium chloride in the ordered cubic phase  $T_d^1$ . \*

Point in the Brillouin zone	Group of k	Optical branches	Acoustical branches
F	$T_d$	$F_2(LO, TO)^{\dagger}$	$F_2$ (pure translation)
R	$T_d$	$F_2(LO, TO)$	$F_2(LA, TA)$
X	$D_{2d}$	$B_2(LO) + E(TO)$	$A_1(LA) + E(TA)$
M	$D_{3d}$	$B_2(T_2O) + E(LO, T_1O)$	$A_1(T_2A) + E(LA, T_1A)$
$\Lambda$	$C_{3v}$	$A_1(LO) + E(TO)$	$A_1(LA) + E(TA)$
$\Delta$	$C_{2v}$	$A_1(LO) + B_1, B_2(TO)^{\oplus}$	$A_1(LA) + B_1, B_2(TA)^{\oplus}$
$\Sigma$	$C_s$	$A'(LO) + A'(T_2O) + A''(T_1O)$	$A'(LA) + A'(T_2A) + A''(T_1A)$
ST <sup>⊗</sup>	$C_{2v}$	$A_1 + B_1, B_2^{\oplus}$	$A_1 + B_1, B_2^{\oplus}$
S, C <sup>⊗</sup>	$C_s$	$2A' + A''$	$2A' + A''$
Z	$C_2$	$A + 2B$	$2A + B$
k <sup>⊗</sup>	$C_1$	3	3

\* See Ref. 14. The labels of the optical and acoustical branches have been interchanged with respect to Ref. 14, because of a change of origin (see text).

<sup>†</sup> The  $F_2$  optical modes are split by the macroscopic electric field.

<sup>⊕</sup>  $B_1, B_2$  modes are degenerate in pairs owing to time-reversal symmetry.

<sup>⊗</sup> C is any point on the symmetry planes

k is any point in the Brillouin zone.

TABLE III - Space group reduction coefficients for the ammonium halide lattice

$T_d^1$ .

Point in the Brillouin zone	Wave vector group representations	Space group representations				
		$A_1$	$A_2$	E	$F_1$	$F_2$
$\Gamma, R$	$A_1$ $A_2$ E $F_1$ $F_2$	1	1	1	1	1
$X, M$	$A_1$ $A_2$ $B_1$ $B_2$ E	1	1	1	1	1
$\Delta, T$	$A_1$ $A_2$ $B_1$ $B_2$	1	1	1	1	1
$A$	$A_1$ $A_2$ E	1	1	1	1	1
$\Sigma, S, C$	$A'$ $A''$	1	1	1	1	2
$Z$	A B	1	1	2	1	1
k		1	1	2	3	3

TABLE IV - Raman selection rules of the optical and acoustical branches of the dispersion curves for the ammonium halides in the disordered phase II.

Points in the Brillouin zone	Optical branches	Polarization character	Acoustical branches	Polarization character
$\Gamma$	LO, TO <sup>*</sup>	F	pure translation	-
R	LO, TO	F	LA, TA	F
X	LO TO	F F	LA TA	$\Lambda + E$ F
M	T <sub>2</sub> O LO, T <sub>1</sub> O	F F	T <sub>2</sub> $\Lambda$ LA, T <sub>1</sub> $\Lambda$	$\Lambda + E$ F
$\Lambda$	LO TO	$\Lambda + F$ E + F	LA TA	$\Lambda + F$ E + F
$\Delta$	LO TO <sup>†</sup>	$\Lambda + E + F$ F	LA TA <sup>†</sup>	$\Lambda + E + F$ F
$\Sigma$	LO T <sub>1</sub> O T <sub>2</sub> O	$\Lambda + E + F$ E + F $\Lambda + E + F$	LA T <sub>1</sub> $\Lambda$ T <sub>2</sub> $\Lambda$	$\Lambda + E + F$ E + F $\Lambda + E + F$
T	O <sub>1</sub> , O <sub>2</sub> <sup>†</sup> O <sub>3</sub>	F $\Lambda + E + F$	$\Lambda_1, \Lambda_2$ <sup>†</sup> $\Lambda_3$	F $\Lambda + E + F$
S, C	O <sub>1</sub> O <sub>2</sub> O <sub>3</sub>	$\Lambda + E + F$ $\Lambda + E + F$ E + F	$\Lambda_1$ $\Lambda_2$ $\Lambda_3$	$\Lambda + E + F$ $\Lambda + E + F$ E + F
Z	O <sub>1</sub> O <sub>2</sub> O <sub>3</sub>	F $\Lambda + E + F$ F	$\Lambda_1$ $\Lambda_2$ $\Lambda_3$	$\Lambda + E + F$ F $\Lambda + E + F$

TABLE IV - (continued)

k	$O_1$	$A + E + F$	$\Lambda_1$	$A + E + F$
	$O_2$	$A + E + F$	$\Lambda_2$	$A + E + F$
	$O_3$	$A + E + F$	$\Lambda_3$	$A + E + F$

\* The LO, TO mode at the  $\Gamma$  point is split by the macroscopic electric field.

† Modes degenerate in pairs owing to time-reversal symmetry.

TABLE V - Raman selection rules of the optical and acoustical branches of the dispersion curves for the ammonium halides in the disordered phase I.

Points in the Brillouin zone	Optical branches	Polarization character	Acoustical branches	Polarization character
$\Gamma$	LO, TO <sup>*</sup>	F	pure translation	-
X	LO	F	LA	F
	TO	F	TA	F
L	LO	F	LA	A + E
	TO	F	TA	F
W	O <sub>1</sub>	A + E	A <sub>1</sub>	A + E
	O <sub>2</sub>	F	A <sub>2</sub>	F
$\Delta$	LO	A + E + F	LA	A + E + F
	TO	F	TA	F
$\Lambda$	LO	A + F	LA	A + F
	TO	E + F	TA	E + F
E, K, U, S	O <sub>1</sub>	A + E + F	A <sub>1</sub>	A + E + F
	O <sub>2</sub>	E + F	A <sub>2</sub>	E + F
	O <sub>3</sub>	A + E + F	A <sub>3</sub>	A + E + F



TABLE V - (continued)

Z	$O_1$	$\Lambda + E + F$	$\Lambda_1$	$\Lambda + E + F$
	$O_2$	F	$\Lambda_2$	F
	$O_3$	F	$\Lambda_3$	F
Q	$O_1$	$\Lambda + E + F$	$\Lambda_1$	$\Lambda + E + F$
	$O_2$	$\Lambda + E + F$	$\Lambda_2$	$\Lambda + E + F$
	$O_3$	$\Lambda + E + F$	$\Lambda_3$	$\Lambda + E + F$
k	$O_1$	$\Lambda + E + F$	$\Lambda_1$	$\Lambda + E + F$
	$O_2$	$\Lambda + E + F$	$\Lambda_2$	$\Lambda + E + F$
	$O_3$	$\Lambda + E + F$	$\Lambda_3$	$\Lambda + E + F$

\* The LO, TO mode at the  $\Gamma$  point is split by the macroscopic electric field.

TABLE VI - Possible assignments of the peaks observed on the Raman spectra of ammonium halides in phase II.

Halide	Frequency ( $\text{cm}^{-1}$ )	Observed polarization	Possible assignment
$\text{NH}_4\text{Cl}$	95	A + E	$T_2 A(M)$
	115	F	LA, $T_1 A(M)$ ; TA(X)
	145	F	$T_2 O(M)$ ; TO(X)
	170	F	TO(F); LO, TO(R); LO, $T_1 O(M)$
	195	F	LO, $T_1 O(M)$ ; LO(X)
$\text{NH}_4\text{Br}$	56	$A(?) + E$	$T_2 A(M)$
	~80	F	LA, $T_1 A(M)$ ; TA(X)
	137	F	$T_2 O(M)$ ; TO(X)
	180	F	LO, $T_1 O(M)$ ; LO(X)
$\text{NH}_4\text{I}^*$	125	-	$T_2 O(M)$ ; TO(X)
	160	-	LO, $T_1 O(M)$ ; LO(X)

\* See Ref. 20.